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Fate of Chlorsulfuron in the Environment. 1. Laboratory Evaluations

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Abstract: The behaviour and fate of chlorsulfuron in aqueous and soil systems were examined in laboratory studies. Aqueous hydrolysis was pH-dependent and followed pseudo-first-order degradation kinetics at 25°C, with faster hydrolysis occurring at pH 5 (half-life 24 days) than at either pH 7 or 9 (half-lives >365 days). Degradation occurred primarily by cleavage of the sulfonylurea bridge to form the major metabolites chlorobenzenesulfonamide (2-chlorobenzenesulfonamide) and triazine amine (4-methoxy-6-methyl-1,3,5-triazin-2-amine). This route is a major degradation pathway in water and soil systems. Aqueous photolysis (corrected for hydrolysis) proceeded much more slowly (half-life 198 days) than aqueous hydrolysis and is not expected to contribute significantly to overall degradation. Hydrolysis in soil thin-layer plates exposed to light (half-life 80 days), however, progressed at a much faster rate than in dark controls (half life 130 days), which suggests that a mechanism other than direct photolysis may have been operative. An aerobic soil metabolism study (25°C) in a Keyport silt loam soil (pH 6·4, 2·8% OM) showed that degradation was rapid (half-life 20 days). Dissipation in an anaerobic sediment/water system (initial pH of water phase 6·7, final pH 7·4) progressed much more slowly (half-life >365 days) than in aerobic soil systems. Major degradation products in aerobic soil included the chlorobenzenesulfonamide and triazine amine as in the aqueous hydrolysis study. Neither of these degradation products exhibited phytotoxicity to a variety of crop and weed species in a glasshouse experiment, and both exhibited an acute toxicological profile similar to that of chlorsulfuron in a battery of standard tests. Demethylation of the 4-methoxy group on the triazine moiety and subsequent cleavage of the triazine ring is another pathway found in both aqueous solution and soils, though different bonds on the triazine amine appear to be cleaved in the two systems. Hydroxylation of the benzenesulfonamide moiety is a minor degradation pathway found in soils. Two soils amended with 0·1 and 1·0 mg kg^{-1} chlorsulfuron showed slight stimulation of nitrification. The 1·0 mg kg^{-1} concentration of chlorsulfuron resulted in minor stimulation and inhibition of ^{14}C-cellulose and ^{14}C-protein degradation, respectively, in the same soils. Batch equilibrium adsorption studies conducted on four soils showed that adsorption was low in this system (K_{oc} 13–54). Soil thin-layer chromatography of chlorsulfuron (R_f = 0·55–0·86) and its major degradation products demonstrated that the chlorobenzenesulfonamide (R_f = 0·34–0·68) had slightly less mobility and that the triazine amine (R_f = 0·035–0·40) was much less mobile than chlorsulfuron. In an aged column leaching study, subsamples of a Fallsington sandy loam (pH_{water} 5·6, OM 1·4%) or a Flanagan silt loam (pH_{water} 6·4, OM 4·0%) were treated with chlorsulfuron, aged moist for 30 days in a glasshouse and then placed upon a prewet column of the same soil type prior to initiation of leaching. This treatment resulted in the retention of much more total radioactivity (including degradation products) than by a prewet column, where initiation of leaching began immediately after chlorsulfuron application, without aging (primarily chlorsulfuron parent). © 1998 SCI

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Key words: adsorption; chlorsulfuron; degradation; degradation products; dissipation; environmental fate; hydrolysis; leaching; sulfonylureas

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1 INTRODUCTION

Chlorsulfuron (1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea was the first sulfonylurea herbicide sold for use in row crops, entering selected cereal markets in 1981.[1] It has gained broad acceptance primarily in the cereals market world-wide, with over 6 million hectares treated in 1995 (Saladini, J. L., DuPont Company, 1997, pers. commum.) and is used in both pre- and post-emergent applications at labeled rates of 4–18·75 g AI ha^{-1}. It is also used at higher rates (157·5 g AI ha^{-1}) for non-crop industrial and industrial turf weed control. Because chlorsulfuron was in the vanguard of a new class of herbicide chemistry with unique attributes such as low-dose chemistry,[2,3] it has generated a great deal of research interest. Several reviews have been published which offer more extensive listings of articles for further reading. The discovery, physical and chemical properties, toxicology, mode of action, and plant uptake and metabolism have been covered in several papers.[1,4–7] The soil behavior of chlorsulfuron has also been reviewed.[5,6,8–10] The influence of certain key chemical and physical properties of chlorsulfuron (Table 1) on its behavior in the environment is well-documented and has been discussed in many of the previously cited papers.

Paramount to comprehending its behavior in the environment is an understanding of the chemical state of the active molecule. With a pK_a of 3·6 (Table 1), (**1**) chlorsulfuron (Fig. 1) is a weak acid which exists primarily as a negatively charged species at pH values of the soil solution found in normal agronomic soils. The balance of species become progressively more protonated, and thus uncharged, in more acidic solutions. This property results in increased solubility in neutral and alkaline solutions versus more acidic solutions and results in large differences in K_{ow} with pH. Its relatively high water solubility and predominantly negatively charged state indicate the potential for chlorsulfuron to be mobile in most mineral soils, whose surface matrices are predominantly negatively charged and whose voids are filled with an aqueous solution consisting of a multitude of ions, dissolved salts and other minerals organic materials derived from various sources.[11] Chlorsulfuron has been described in several laboratory studies as having low to moderate adsorption to soils and various soil constituents and having high to moderate mobility potential in soils, influenced by pH.[4,8,12,15–23]

The purpose of this paper and the companion paper on field studies[24] is to present data on the environmental fate and mobility of chlorsulfuron which have not previously been published and which supplement the current body of knowledge. This paper also attempts to integrate key information from other publications. The data are derived from laboratory studies reported in unpublished DuPont internal publications.

2 EXPERIMENTAL PROCEDURES

2.1 Aqueous hydrolysis study and direct aqueous photolysis study

For the aqueous hydrolysis study (Dietrich, R. F. & McAleer, N. C., Hydrolysis of [*phenyl-U*-^{14}C]chlorsul

TABLE 1
Selected Chemical and Physical Properties of Chlorsulfuron[a]

Molecular formula		$C_{12}H_{12}ClN_5O_4S$
Relative molecular mass		357·78
Melting point		174–178°C
Vapor pressure (25°C)		$2·3 \times 10^{-11}$ mm Hg
Henry's Law constant (25°C)		$1·02 \times 10^{-13}$ atm-m^3 mol^{-1}
Dissociation constant (pK_a)		3·6
Octanol/water partition coefficient (25°C) K_{ow}		
pH 5		2·13
pH 7		0·10
pH 9		0·04
Solubility in:	at temperature of (°C):	g $liter^{-1}$
Acetone	22	57
Hexane	22	<0·01
Methanol	22	14
Methylene chloride	22	102
Toluene	22	3
Water (distilled, deionized)	25	0·1–0·125
Water (unbuffered)		
pH 5	25	0·59
pH 7	25	31·8
Xylene	—	0·2

[a] Summarized from Reference 13.

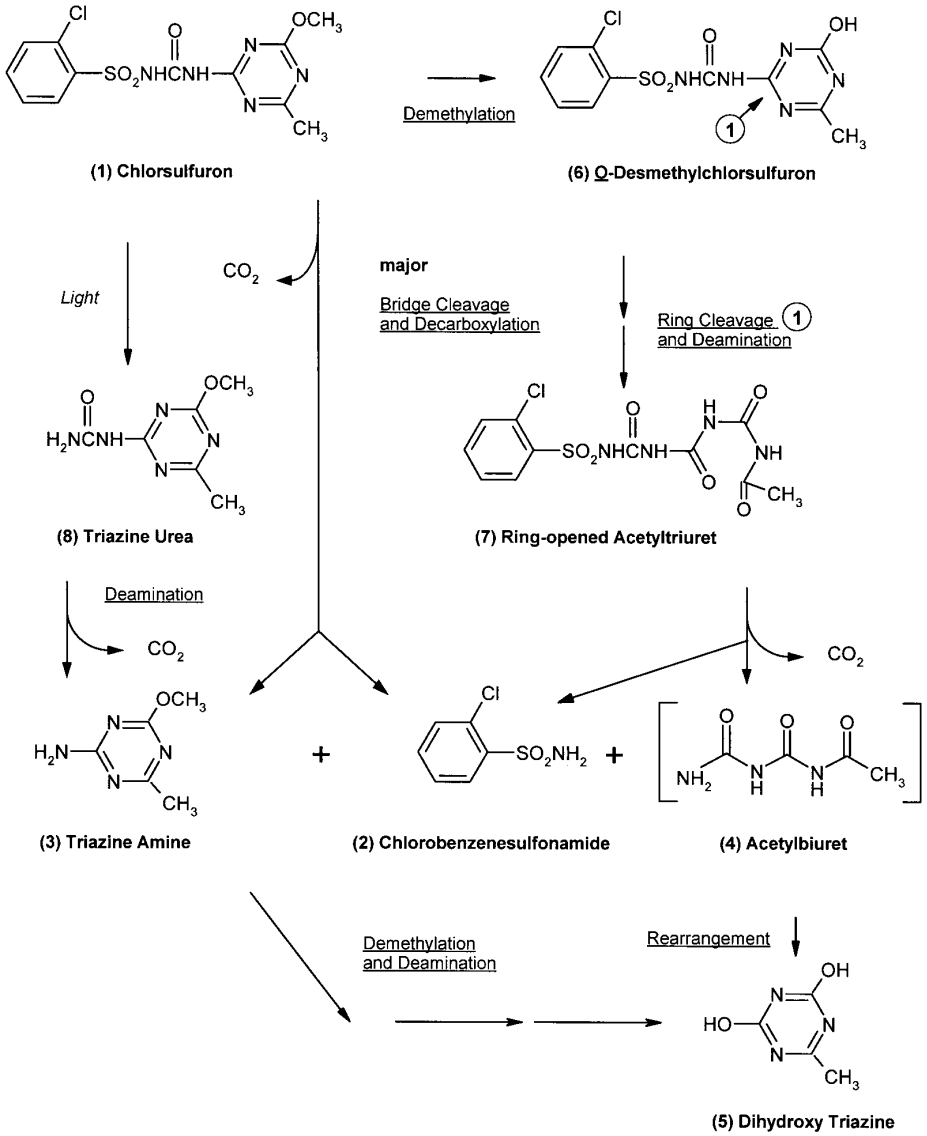

Fig. 1. Proposed hydrolytic degradation pathways for chlorsulfuron at pH 5.

furon and [*triazine*-2-^{14}C]chlorsulfuron. *DuPont Internal Report*, AMR 1455-89, 1989), test solutions (final chlorsulfuron concentration approximately 5 mg litre^{-1}) were prepared in flasks (1 litre) for each radioisotope by mixing approximately 0·8 ml stock solutions of [*triazine*-2-^{14}C]chlorsulfuron (specific activity 563 kBq mg^{-1}, purity >95%) or [*phenyl-U*-^{14}C]chlorsulfuron (specific activity 426 kBq mg^{-1}, purity >95%) in pH 7 sodium phosphate (monobasic) buffer with 500 ml of pH 5 acetate (glacial acetic acid) buffer, pH 7 sodium phosphate buffer, pH 9 borate (boric acid) buffer. All buffers were 0·01 M and were adjusted with 1 M sodium hydroxide to their respective pH levels. The flasks were maintained at 25(±1)°C in an incubator in the dark. On days 0, 3, 7, 14, 21 and 31, single 5-ml aliquots of solution were removed for analysis. Total radioactivity was measured for triplicate 100-µl aliquots by liquid scintillation counting (LSC) in 15 ml of scintillation cocktail (NEN Formula 989, New England Nuclear Products, Billerica, MA) on a Mark III Liquid Scintillation Counter, Model 6881 (TM Analytic, Inc., Elk Grove, IL). The relative proportions of parent compound and major radiolabeled degradation products were determined by HPLC (HPLC: Varian Vista 5560, Varian Associates, Palo Alto, CA; injection volume: 500 µl; column: 4·6 mm × 25 cm Zorbax® RX (MAC MOD Analytical, Inc., Chadds Ford, PA); guard column: 4·6 × 30 mm RP-18 (Brownlee Labs, Emeryville, CA); temp. 40°C; mobile phases: (A) acetonitrile + 0·1% H_3PO_4 (1 + 1 by volume), (B) water + 0·1% H_3PO_4 (1 + 1 by volume); gradient (minutes/%A): 0–1/0, 1–31/45, 31–35/100, 35–37/0). Nonradioactive standards were monitored by UV absorbance detected by a Varian UV-200 variable-wavelength detector. The elution of radioactivity was monitored with a Raytest Ramona-LS radiochemical detector (IN/US Service Corporation, Fairfield, NJ) equipped with a 0·2-ml CaF_2 flow cell (IN/US Service

Corporation, Fairfield, NJ). Chemicals used were reagent grade or better. Distilled water was further purified in a Milli-Q® water purification system (Millipore Corporation, Bedford, MA). Individual radiolabeled degradation products from the pH 5 test solutions were purified by collecting fractions from multiple HPLC injections (Rainin Instrument Co., Woburn, MA) Rabbit® HPLC system, (column: Dynamax-60A 8 μm C18, 21·4 mm ID × 5 cm (Dynamax, Inc., Houston, TX); mobile phases (A) acetonitrile + 0·1% formic acid (1 + 1 by volume) and (B) water + 0·1% formic acid (1 + 1 by volume); gradient (minutes/%A): 0–20/0, 20–20·5/10, 20·5–40/10, 40–40·5/20, 40·5–60/20, 60–60·5/30, 60·5–80/45, 80–80·5/45, 80·5–120/45). Identification of the purified chlorsulfuron hydrolysis products was achieved using micro-column liquid chromatography/continuous-flow fast atom bombardment mass spectrometry. For detailed discussion of the methods employed, see Reiser *et al.*[25] and Shalaby *et al.*[26]

2.2 Direct aqueous photolysis study

The direct aqueous photolysis experiments (Dietrich, R. F. & McAleer, N. C., Photodegradation of [*phenyl*-U-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C]chlorsulfuron in water conducted in sunlight. *DuPont Internal Report*, AMR 1455-89.161-2, 1989) were conducted using the same stocks of [*triazine*-2-^{14}C]- and [*phenyl-U*-^{14}C]chlorsulfuron as used for the aqueous hydrolysis experiments. Test solutions of approximately 5 mg litre^{-1} were placed in water-jacketed beakers under sterile conditions and covered with quartz lids to prevent evaporation and permit ultraviolet (UV) light transmission. The beakers were maintained at 25(±1)°C and placed in natural sunlight in Wilmington, DE during the period 23 June–24 July 1989. Cumulative global radiation (285–2800 nm) and UV radiation (290–385 nm) striking the vessel were monitored respectively with an EPLAB Model 8-48 Black and White Pyranometer and EPLAB Ultra-violet Radiometer attached to an EPLAB Model 415-6630 Electronic Integrator (Eppley Laboratory, Inc., Newport, RI). Total radioactivity and characterization of the major radiolabeled degradation products were performed using the same methodology as in the aqueous photolysis experiments.

2.3 Soil surface photolysis

Soil surface photolysis experiments (Hawkins, D. R., Kirkpatrick, D., Dean, G. M. and Mellor, S. J., The photodegradation of ^{14}C-chlorsulfuron on a silty clay loam soil. *DuPont Internal Report*, AMR 1563-89, 1989) were conducted using the same lots of [*triazine*-2-^{14}C]- and [*phenyl-U*-^{14}C]chlorsulfuron as used for the aqueous hydrolysis and direct aqueous photolysis experiments. Separate stock solutions were made in water. The test soil was a Nora silty clay loam collected from Walthill, Nebraska–20% sand, 52% silt, 29% clay, 2·0% OM, CEC 19·6 meq 100 g^{-1}, pH_{water} 8·0. Aliquots (0·1 ml of the [^{14}C]chlorsulfuron treatment solution (0·16 mg litre^{-1}) were applied evenly to the surface of thin soil layers *c.* 1 mm thick and 2·5 × 4 cm supported by glass plates. Multiple soil plates were irradiated simultaneously for approximately 12 h in every 24 h using a Suntest Accelerated Exposure Unit (Heraeus Equipment Limited, Brentwood, Essex, UK) fitted with a xenon arc light source, whose spectrum approaches that of natural sunlight. A system of mirrors and filters prevented ultra-violet radiation with a wavelength of <290 nm from reaching the soil surfaces. Dark control samples received the same treatment as the irradiated samples except for exposure to light. The plates were maintained at 25(±5)°C during irradiation and 15–22°C during dark periods in a ventilated container cooled with circulating water. Volatile photodegradation products were trapped by drawing a stream of humidified air through the system at a rate of 40–50 ml min^{-1} through polyurethane foam bungs, followed by trap solutions of ethylene glycol and potassium hydroxide. Following 0, 1, 3, 7, 14, 21 and 31 days of exposure, the soil from duplicate plates was scraped off and shaken with acetone + 0·1 M aqueous ammonium carbonate (9 + 1 by volume; 10 ml) for *c.* 20 min at ambient temperature to extract radioactivity. If the total recovery of applied radioactivity was <90%, the soil was agitated in 0·1 M aqueous ammonium carbonate for 1 h in an ultrasonic water bath at 50°C. Following centrifugation at 2500 rev min^{-1} for *c.* 15 min, radioactivity in the extracts was measured in duplicate by LSC (LKB Model 1219 RackBeta Spectral Counter, LKB Wallace, Türku, Finland) using MI-31 scintillation cocktail (Canberra Packard Instrument Co., Ltd, Pangbourne, Berks., UK). Radioactivity remaining on the soil (air-dried overnight) was measured by combustion of triplicate aliquots in an automatic sample oxidizer (Canberra Packard Tricarb®, Model 306 Mark II), using a trapping solution of Optisorb I and mixing with Optisorb S scintillation counting (Fisons plc., Loughborough, UK) prior to LSC counting. The foam bungs were extracted twice with acetone + 0·1 M aqueous ammonium carbonate (9 + 1 by vol; *c.* 40 ml for ~10 min in an ultrasonic bath, pooled, and duplicate 0·5-ml aliquots were counted by LSC. Duplicate 1-ml aliquots of the ethylene glycol and NaOH trapping solutions were mixed respectively with 1 ml of methanol or water and measured for radioactivity by LSC.

Chromatographic analysis was conducted on pooled extracts concentrated by rotary evaporation and reconstituted with water, then analyzed by HPLC (HPLC: Waters Model 510 pumps, Model 660 gradient controller, U6K injector (Waters, Milford, MA), Model 484 variable wavelength detector set at 254 nm (Millipore (UK), Ltd) and a Ramona 5 radioactivity detector

(Raytest Instruments, Ltd, Sheffield, UK); column: DuPont Zorbax Rx, 4·6 ID × 250 mm; mobile phases: (A) water + 0·1% phosphoric acid (1 + 1 by volume) and (B) acetonitrile + 0·1% phosphoric acid (1 + 1 by volume); gradient (minutes/%A): 0/100, 1/100, 31/55, 33/0, 35/0, 36/100, 46/100. One-minute fractions of column eluate were collected for 46 min after injection to check the recovery of radioactivity from the column and to qualify unchanged chlorsulfuron and the degradation products present in the extracts. Non-radiolabeled reference compounds were synthesized and their retention times compared with those of degradation products to identify the latter.

2.4 Aerobic soil degradation

2.4.1 [^{14}C]-*Chlorsulfuron aerobic soil metabolism study* The aerobic soil degradation experiments (Rapisarda, C., Han, J. C-Y. & Smith, G. A., Microbial activity in soils treated with chlorsulfuron. *DuPont Internal Report*, AMR 88-82, 1982, in rewritten form with greater elucidation of degradation product structures as Priester, T. M., Aerobic soil metabolism of chlorsulfuron. *DuPont Internal Report*, AMR 2213-91, 1991) with [*phenyl-U*-^{14}C]chlorsulfuron (222 kBq mg^{-1}, >99% purity) and [*triazine*-2-^{14}C]chlorsulfuron (563 kBq mg^{-1}, 98% purity) were conducted in biometer flasks described in Bartha and Pramer.[27] Fresh soil collected from fields with no history of herbicide treatment was passed through a 2-mm screen prior to use. The test soil was a Keyport silt loam collected in Newark, Delaware with 21% sand, 62% silt, 17% clay, 2·75% OM, a CEC of 8·2 meq 100 g^{-1}, and pH_{water} of 6·4. An aqueous solution of [^{14}C]chlorsulfuron was added to 50 g soil and mixed to give a concentration of 0·1 mg kg^{-1}, and water was added to reach 18·2% (by weight), equivalent to 70% of field capacity. This concentration is approximately five times the maximum Glean® FC rate for cereal crops assuming an even distribution through a depth of 10 cm in a soil of 1·3 g cm^3 bulk density, or equal to the maximum Telar® rate for industrial weed control through a depth of 2 cm. The flasks were stoppered and purged with a constant, humidified oxygen stream and allowed to incubate at 25°C in the dark. [^{14}C] carbon dioxide escaping the soil was trapped in sodium hydroxide, which was sampled and replaced at two-week intervals. Aliquots (0·5 ml) were counted by LSC (New England Nuclear Scintillation Cocktail Formula 947; either Searle Model 6881, Searle Analytic, Chicago, Illinois or Isocap 300 liquid scintillation spectrometer). To determine the amount of chlorsulfuron degradation, two replicate biometer flasks were withdrawn from the incubator following 0, 6, 8, 12, 15, 30, 45, 60, 90, 120 and 180 days of incubation. Each soil was extracted three times with dichloromethane + acetone (1 + 1 by volume), three times with methanol + 0·08 M ammonium hydroxide (1 + 1 by volume), and three times with 0·01 M sodium hydroxide. The pooled extract was acidified with 1 M hydrochloric acid to pH 5 and partitioned with dichloromethane, counted by LSC, and then reduced to 1–2 ml for TLC analysis. The TLC plates (250 and 500 μm, Merck Kieselgel F-254, E. Merck, Darmstadt, Germany) were developed to 15 cm with dichloromethane + acetone + methanol + 9 M ammonium hydroxide (15 + 27 + 15 + 3 by volume) and were compared to standards of chlorsulfuron and possible degradation products. For GC/MS identification, fractions were scraped and extracted four times with dichloromethane + acetone or methanol + 0·04 M ammonium hydroxide (1 + 1 by volume), depending on polarity of the compound. Radioactive areas of interest were located on the TLC plates by autoradiography. The degradation products were directly analyzed by GC/MS (Perkin Elmer Model 990, Perkin Elmer Corporation, Norwalk, CT), 0·2 cm ID × 60 cm column packed with 10% OV-1 on 80–100 mesh Chromosorb W-HP, programmed from 100 to 250°C at 8°C min^{-1}.

Intact chlorsulfuron and polar degradation products were methylated with diazomethane prior to GC/MS analysis. Extracted soil samples were oven-dried at 50°C for two days, homogenized and 0·2–0·3-g subsamples were analyzed for radioactivity by combustion (Packard Model 306 Sample Oxidizer, Packard Instruments Company, Meriden, CT).

2.4.2 [^{14}C]*Triazine amine soil metabolism study*
The degradation study with the triazine amine (Rhodes, B. C., Aerobic soil metabolism of [2-^{14}C] 4-methoxy-6-methyl-1,3,5-triazin-2-amine. *DuPont Internal Report*, AMR 418-85, 1985) was conduced using Keyport silt loam soil (different from the one described in Section 2.4.1) collected in Newark, Delaware with 11% sand, 78% silt, 11% clay, 4·7% OM, a CEC of 14·1 meq 100 g^{-1} and pH_{water} of 4·3. An aqueous solution of [2-^{14}C]4-methoxy-6-methyl-1,3,5-triazin-2-amine (1010 kBq mg^{-1}), was added to 50 g soil contained in a biometer flask to give a concentration of 0·1 mg kg^{-1}. The methodology employed was similar to that in the aerobic soil metabolism study (Section 2.4.1), except that sampling occurred after 4, 10, 17, 30, 61, 91, 122, 183, 243, 365 and 456 days after treatment. LSC counting was done using a Tracor Analytic® Mark III liquid scintillation counter using NEN Atomlight® cocktail. The soil was extracted (first extraction) four times (shaken for 0·15 min) with methylene chloride + methanol + 9 M sodium hydroxide (75 + 20 + 0·5 by volume; *c.* 150 ml), centrifuged and the supernatant filtered. The extracts were pooled and reduced to 1–2 ml by rotary evaporation at 40°C under a nitrogen stream. The remaining soil was extracted three times (second extraction) with 0·1 M sodium hydroxide (shaken for *c.* 15 min). The extracts were

pooled, neutralized with phosphoric acid, and partitioned three times with ethyl acetate. The ethyl acetate was evaporated to 1–2 ml and the aqueous phase was concentrated to 1–2 ml by rotary evaporation at 40°C. The remaining soil was subjected to a final extraction (third) by adding 1 M sodium hydroxide (*c.* 150 ml), refluxing for 1 h and reducing to 1–2 ml. The remaining soil pellet was air-dried, ground with a mortar and pestle, and triplicate 2-g aliquots were combusted on a OX-300 Oxidizer (R. J. Harvey Instrument, Co., Hillsdale, NJ) using NEN Oxifluor®-CO_2 and counted by LSC. The concentrated sample from the first extraction and the concentrated ethyl acetate phase from the second extraction were analyzed by TLC. The plates (250 and 500 μm, Merck Kieselgel F-254) were developed to 15 cm using methylene chloride + methanol + 1 M ammonium hydroxide (145 + 50 + 5 by volume). Nonradiolabeled reference standards were visualized on developed plates by fluorescence quenching. Radioactive bands were detected and integrated on a Berthold Model LB2832 Automatic TLC-Linear Analyzer (EG&G Berthold, Bad Wildbad, Baden-Württemberg, Germany). The concentrated aqueous phase of the second extraction and the concentrated sodium hydroxide sample from the third extraction were analyzed by HPLC (Hewlett Packard 1090 LC, Hewlett Packard Co., Wilmington, DE; column: Zorbax® ODS, 4·6 mm × 25 cm, with C_8 guard column; temp. 37°; detector wavelength 254 nm; mobile phases: (A) 0·05 M aqueous ethanol, (B) acetonitrile; gradient (min/%B): 0–4/0, 4–5/0–5, 5–34/5, 34–35/5–0, 35–37/0). Radiochromatograms of these aqueous solutions were obtained by LSC of 1-min/eluate fractions collected on an ISCO Foxy® fraction collector (ISCO, Inc., Lincoln, Nebraska). Identification of radioactive peaks was made by comparison of retention times with those of chromatographed nonradiolabeled standards of suspected degradation products.

2.4.3 Effect of chlorsulfuron on soil microbiol processes

Using a previously described experimental set-up,[28] a study was conducted to ascertain the effect of chlorsulfuron on certain soil microbial processes (Rapisarda *et al.*, 1982, full reference in Sect. 2.4.1). Duplicate 50-g samples of Keyport silt loam identical to that used in Section 2.4.1. and a Fallsington study loam soil collected in Glasgow, Delaware with 56% sand, 29%, silt, 15% clay, 1·4% OM, a CEC of 4·8 meq 100 g^{-1} and pH_{water} of 5·6, were added to flasks and were allowed to equilibrate for a two-week period. They were then treated with 0·1 or 1·0 mg kg^{-1} of non-radiolabeled technical grade (purity >95%) chlorsulfuron dissolved in water buffered to pH 7, and 200 mg kg^{-1} of nitrogen as ammonium sulfate was added to each flask. Flasks without chlorsulfuron and with nitrogen, or without either were included as controls. The flasks were incubated at 35°C for 70 days. The nitrate concentration of a filtered water extract of the soil (100 ml water, ultrasonicated for 30 min) was measured using a nitrate electrode (Orion Nitrate Ion Activity Electrode, Model 92-07; Orion Research, Boston, MA; Corning Model 12 pH Meter, Corning, Inc., Corning, New York). In a separate experiment, similar to the nitrification experiment, 50 g of soil was fortified with [^{14}C]cellulose (100 mg, 0·296 kBq mg^{-1}), treated with either 0 or 1·0 mg kg^{-1} of non-radiolabeled technical grade (purity >95%) chlorsulfuron, incubated in the dark at 25°C, and escaping carbon dioxide was trapped in sodium hydroxide solutions. Subsamples were drawn from the traps over a period of 60 days and counted by LSC to ascertain the percentage of radioactivity escaping as [^{14}C]carbon dioxide. An additional set of flasks fortified with ^{14}C-algal protein in yeast extract (50 mg, 0·148 kBq mg^{-1}) was treated with either 0 or 1·0 mg kg^{-1} of non-radiolabeled technical grade (purity >95%) chlorsulfuron, and incubated and counted by LSC as in the [^{14}C]cellulose degradation experiment. Subsamples from the sodium hydroxide traps were drawn over a period of 30 days to determine the percentage of radioactivity escaping as [^{14}C]carbon dioxide.

2.5 Anaerobic soil/aquatic sediment study

For the anaerobic soil/aquatic sediment study (Chrzanowski, R. L. & Priester, T. M., Degradation of ^{14}C-DPX W4189 in anaerobic aquatic environments. *DuPont Internal Report*, AMR 38-81 (91) Rev. 1, 1991) sediment and water were collected from the bottom of a spring-fed pond located in Landenberg, Pennsylvania. The sediment was characterized as having 25% sand, 74% silt, 1% clay, 3·7% OM, a CEC of 11·0 meq 100 g^{-1} and pH_{water} of 5·6. Its properties are similar to the Keyport silt loam soil used in the aerobic soil degradation studies. The test system consisted of 50 g of sediment in a glass centrifuge bottle to which 1 g of freshly cut alfalfa was added along with 100 ml of pond water. The system was purged with filtered nitrogen gas, tightly capped, and placed in a dark incubator maintained at 25(±1)°C to achieve anaerobicity. Solutions of 150 μg of [*triazine*-2-^{14}C]chlorsulfuron (specific activity 563 kBq mg^{-1}, purity >96%) or [*phenyl-U*-^{14}C]chlorsulfuron (specific activity 222 kBq mg^{-1}, purity = 97%) in methylene chloride were added to the test systems, and if maintained under sterile conditions, 0·1% sodium azide was added to autoclaved bottles according to the method of Miyazaki *et al.*[29] Although not continuously purged with nitrogen gas, recovery of total radioactivity (from the water and sediment) averaged 99·8(±4·3)% over all treatments, demonstrating minimal potential for loss of volatile products. Oxygen levels remained below 0·05 mg $litre^{-1}$ in all samples for the duration of the experiment. Samples were taken fol-

lowing, 0, 7, 18 and 70 days of incubation of the soil treated with [*phenyl-U*-^{14}C]chlorsulfuron and following 0, 14, 56, 112 and 365 days of incubation of the soil treated with [*triazine*-2-^{14}C]chlorsulfuron. Upon conclusion of the incubation period, the bottles were opened, centrifuged at 2000 rev min^{-1} for 10 min, decanted, 50 ml of water were added to the soil, shaken for 1 min, centrifuged again and decanted. The combined water was analyzed for radioactivity by LSC (Formula 947® scintillation cocktail, New England Nuclear; Isocap 300 Scintillation Counter). The radioactivity remaining in the sediment was extracted by adding 5% ammonium carbonate in methanol + water (2 + 1 by volume), heating in a steam bath for 1 h, cooling, centrifuging, decanting, adding 100 ml of methanol, shaking, decanting and combining the supernatants. The resulting solution was concentrated to $<$10 ml volume by rotoevaporation and analyzed by LSC. Subsamples of the extracted sediment were combusted (trapped in Carbo-Sorb® and counted on a Packard Model 306 Biological Oxidizer) to determine the remaining radioactivity. The extracts from water and soil were separately characterized by TLC using 250-μm silica gel chromoplates with fluorescent indicator (Brinkmann Instrument Company, San Gabriel, CA) developed to 15 cm in methylene chloride + methanol + 30% ammonium hydroxide (144 + 50 + 6 by volume) and by autoradiography (SB-5 X-ray film, Kodak, Rochester, NY). Radioactive bands were located with a Berthold Model LB2832 Automatic TLC-Linear Analyzer or by counting ethyl acetate extracts of TLC-plate scrapings using LSC. Comparisons with non-radiolabeled, pure standards visualized by fluorescence quenching (Brinkmann Model CC-20 Chroma-Vue) were used to identify the degradation products.

2.6 Adsorption study

Adsorption/desorption studies (Priester, T. M., Batch equilibrium (Adsorption/desorption) and soil TLC studies with [^{14}C]-chlorsulfuron. *DuPont Internal Report*, AMR 1277-88, 1988) were carried out using published methods[30] using air-dried soils (Table 2) sieved through a 2-mm mesh screen. Aqueous solutions (20 ml) of [*phenyl-U*-^{14}C]chlorsulfuron (specific activity 315 kBq mg^{-1}, purity $>$92%) in 0·01 M calcium sulfate (anhydrous) at initial concentrations of 0·2, 0·5, 1, 2·5 and 6 mg litre^{-1} were added to 20 g of air-dried soil and shaken for 16–24 h in a constant-temperature water bath maintained at approximately 25°C. Preliminary studies showed that both adsorption and desorption had reached pseudoequilibrium by 16 h and that the integrity of the chlorsulfuron was maintained in the solutions. After the equilibration period the soil slurry was centrifuged for 10 min, the supernatant was decanted and filtered, and aliquots were then measured by LSC to determine radioactivity (TM Analytic Model 6881 Mark III liquid scintillation counter). The remaining radioactivity was determined in the soil by combustion (Harvey Model OX300 Oximat® Sample Oxidizer) following one week of air-drying. Desorption of chlorsulfuron was determined using the 6 mg litre^{-1} samples from the adsorption study, replacing the decanted equilibrium solution with fresh 0·01 M calcium sulfate solution, shaking for 16–24 h, centrifuging, decanting and filtering the equilibrium solution and counting aliquots by LSC. The remaining soil was analyzed for total radioactivity by oxidation and LSC. Adsorption and desorption distribution coefficients (K_{ads} and K_{des}) were calculated using the expression

$$C_s = K \times C_e$$

where C_s is the concentration on the soil (mg kg^{-1}), C_e is the equilibrium solution concentration (mg litre^{-1}) and K is the slope of the least-squares regression fit (intercept through zero). K_{ads} and K_{des} values were normalized for organic matter (OM) and organic carbon (OC) by dividing by the fractions of the respective values in Table 2. Freundlich adsorption constants (K_{fads}) were calculated using the rearranged Freundlich

TABLE 2
Selected Soil Characteristics of Soils used for Adsorption/Desorption Studies

	Selected characteristics						
Soil	*Sand*	*Silt*	*Clay* (%)	*OM*	*OC*[a]	*pH*[b]	*CEC* (*meq 100 g*$^{-1}$)
Woodstown sandy loam	60	33	7	1·1	0·6	6·6	5·3
Madera loam	48	35	17	0·8	0·5	8·0	19·6
Keyport silt loam	20	59	21	1·9	1·1	5·7	6·4
Flanagan silt loam	2	81	17	4·3	2·5	5·4	21·1

[a] Calculated using the conversion factor OC = OM × 0·58.
[b] In water.

equation:[31]

$$\log C_s = \frac{1}{n} \log C_e + \log K_{fads}.$$

2.7 Soil thin-layer chromatography (TLC) study

Soil TLC studies (Priester, 1988, full reference in Section 2.6.) were conducted using 400-μm-thick soil plates (20 × 20 cm) using previously described methods[32] on the same soils as in the adsorption/desorption study (Table 2). The [*phenyl-U*-^{14}C]chlorsulfuron was from the same lot as the adsorption/desorption study. The [2-^{14}C]triazine amine (specific activity 678 kBq mg^{-1}, purity >90%) was prepared by New England Nuclear (Boston, Massachusetts) and the [*phenyl-U*-^{14}C]chlorobenzenesulfonamide (specific activity 315 kBq mg^{-1}, purity > 98%) was prepared from the [*phenyl-U*-^{14}C] chlorsulfuron by DuPont. The plates were developed to 10 cm using water, then air-dried for 24 h. Autoradiography (Kodak SB-5 X-ray film) was used to locate the compounds and determine R_f values.

2.8 Saturated column leaching study

In a saturated column leaching study (Chrzanowski, R. L., Soil column leaching studies with ^{14}C-DPX-4189. *DuPont Internal Report*, AMR 26-81, 1981), the mobility of [*phenyl-U*-^{14}C]chlorsulfuron (222 kBq mg^{-1}, >99% purity) was followed in glass columns (5 cm ID × 18 cm length) packed with the Fallsington sandy loam identical to that used in the experiment described in Section 2.4.2 or a Flanagan silt loam collected in Rochelle, Illinois with 5% sand, 64% silt, 31% clay, 4·02% OM, a CEC of 23·4 meq 100-g^{-1} and pH_{water} of 6·7. A 100-g aliquot of soil was treated with an aqueous solution of [^{14}C]chlorsulfuron to give an approximate concentration of 0·45 mg kg^{-1}, placed upon the top of the column and watered immediately to begin percolation ('Fresh' treatment), or wetted to 75% of field capacity (16% and 31% by weight, respectively, for the Fallsington and Flanagan soils), incubated for 30 days in a greenhouse prior to placement on the column and initiation of percolation ('Aged' treatment). The water was percolated continuously through the column for 20 h at a rate of 25·4 mm h^{-1} (508 mm total). Percolate was collected in 5-ml increments and analyzed by LSC (Tracor Analytic® Mark III liquid scintillation counter, New England Nuclear Scintillation Cocktail Formula 947). For the Fallsington soil the percolate was concentrated to 5 ml volume on a rotary evaporator, extracted three times with methylene chloride and ^{14}C-labeled components analyzed by TLC (Brinkmann 250 μ Silica Gel-G chromatoplates) developed in methylene chloride-methanol + hexane (100 + 10 + 10 by volume) to identify the proportion of total radioactivity represented by chlorsulfuron.

2.9 Phytotoxicity of major degradation products

In order to determine the potential biological significance of the major degradation products, chlorobenzenesulfonamide (2-chlorobenzenesulfonamide) and triazine amine (4-methoxy-6-methyl-1,3,5-triazin-2-amine), a screening test was conducted for phytological activity. Pots containing two-week-old plants of selected crop species: soyabean (*Glycine max* (L.) Merr.), cotton (*Gossypium hirsutum* L.), rice (*Oryza sativa* L.), sorghum (*Sorghum vulgare* Pers.), spring wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), and weed species: *Avena fatua* L., *Cyperus rotundus* L., *Digitaria sanguinalis* (L.) Scop., *Echinochloa crus-galli* (L.) P. Beauv., *Ipomoea* sp., and *Xanthium strumatrium* L., or soil planted to their seeds were sprayed with a solution containing either the chlorobenzenesulfonamide or triazine amine (technical-grade of >95% purity dissolved in a mixture of acetone, water and nonionic surfactants) at a rate calculated at on an area basis as 2000 g AI ha^{-1}, and then allowed to grow for three weeks in a glasshouse.

2.10 Statistical analysis and prediction of water solubility

All analyses of variance and statistical comparisons were conducted using the procedure GLM, non-linear regression using the procedure NLIN and correlation using the procedure CORR using SAS software.[33] The water solubility of acetylbiuret (*N*-[[(aminocarbonyl) amino]carbonyl]acetamide; Fig. 1; **4**) was estimated using LogKow and WSKow software programs.

3 RESULTS AND DISCUSSION

3.1 Hydrolytic and aqueous photolytic degradation

3.1.1 Aqueous hydrolysis study

Chlorsulfuron was hydrolysed in a sterile aqueous acetate buffer solution of pH 5 (Section 2.1) and exhibited pseudo-first-order degradation kinetics with an average half-life of 24 days at 25°C (Fig. 2). No significant difference in half-lives between the *triazine*- and *phenyl*-labeled chlorsulfuron was observed ($P \leqq 0{\cdot}01$). The half-life in this study is very close to that of 25 days reported by Dinelli *et al.*,[34] but faster than the 32 days reported by Savin *et al.*[35] in two studies conducted under similar conditions also at pH 5, and significantly

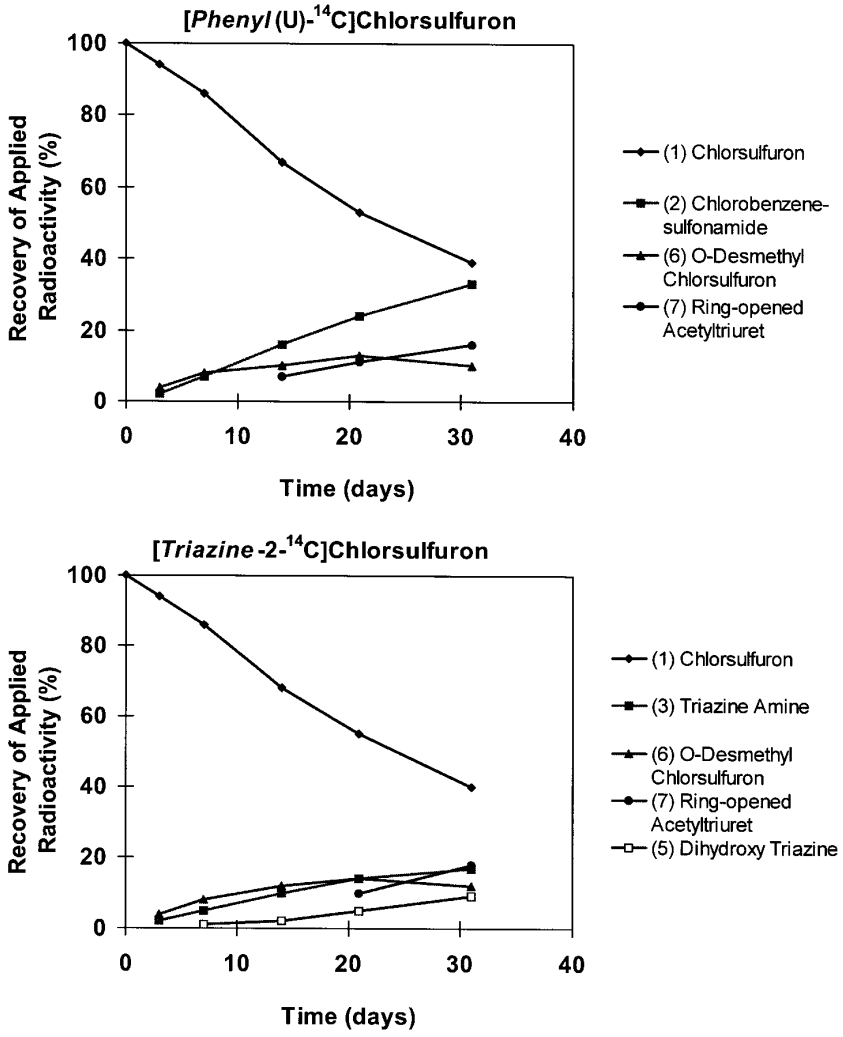

Fig. 2. Hydrolysis of [*phenyl-U*-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C]chlorsulfuron in sterile pH 5 acetate buffer solution at 25°C and formation of degradation products.

longer than the half-life of 16 days reported by Hemmamda *et al.*[36] at pH 5·2. Berger and Wolfe[37] determined a half-life of 5 days in pH 4 buffered water at 22°C. The major degradation products (Fig. 1) identified from [*phenyl-U*-^{14}C]chlorsulfuron following 31 days in the buffer solution were chlorobenzenesulfonamide (2-chlorobenzenesulfonamide; **2**) ring-opened acetyltriuret (1-(2-chlorophenylsulfonyl)-7-acetamido triuret; **7**), and *O*-desmethylchlorsulfuron (1-(2-chlorophenylsulfonyl)-3-(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)urea; **6**), comprising 33, 16 and 10%, respectively, of the total radioactivity at the end of 31 days (Fig. 2). The major degradation products from [*triazine*-2-^{14}C]chlorsulfuron were identified as triazine amine (4-methoxy-6-methyl-1,3,5-triazin-2-amine, **3**), dihydroxy triazine (6-methyl-1,3,5-triazine-2,4-diol, **5**), *O*-desmethylchlorsulfuron (**6**) and ring-opened acetyltriuret (**7**) comprising 17, 8, 12 and 18%, respectively, of the total radioactivity at the end of 31 days. Of the original radioactivity, 39–40% remained as the intact chlorsulfuron for both ^{14}C-radiolabels. Other unidentified radiolabeled components constituted <2% of the recovered radioactivity for either radiolabel.

The major degradation products, chlorobenzenesulfonamide (**2**) and triazine amine (**3**), result from the hydrolytic cleavage of the sulfonylurea bridge, which appears to be the major hydrolytic pathway (Fig. 1), agreeing with the assessments of Hermann *et al.*[38] and Savin *et al.*[35] Hemmamda *et al.*[36] described the mechanism of the formation of (**2**) and (**3**), but did not present any alternative pathways or show degradation to subsequent products. In our studies, (**3**) appears to degrade further through deamination and demethylation to (**5**). The formation of (**6**) is the initial step in another important pathway, in which *O*-demethylation of the methoxy is followed by hydrolytic cleavage of the triazine ring between the 1 and 2 positions (denoted by an encircled '1' on Fig. 1) and subsequent deamination, yielding ring-opened acetyltriuret (**7**). Through subsequent hydrolytic cleavage and decarboxylation, this compound ultimately forms dihydroxy triazine (**5**) and chlorobenzenesulfonamide (**2**). It was speculated that the hydrolytic

cleavage and decarboxylation which produce (**2**) could form the intermediate acetylbiuret (*N*-[[(aminocarbonyl)amino]carbonyl]acetamide; **4**) and subsequently rearranges to produce the dihydroxy triazine (**5**). No (**4**) was found and identified in any of the chlorsulfuron studies, although if formed, it should be relatively stable in solution (Zimmerman, W. T., DuPont Company, 1997, pers. commun.). It was never isolated, possibly because the systems used to separate the degradation products were inadequate for this compound, which is extremely polar and water-soluble (solubility for the neural form predicted as 18 900 mg litre^{-1} using an estimated log K_{ow} of $-0{\cdot}43$).[39] It would tend to elute very quickly, either in the void volume or soon afterwards. Characterization and identification of this proposed degradation product remains an area for future research. Bray *et al.*[40] discuss this possibility but suggest that degradation kinetics point to the likely formation of (**5**) though direct hydrolysis of (**6**). Part of the proposed degradation pathway, including the identification of (**7**), the speculation of the formation of (**4**) and (**2**) and rearrangement to (**5**) have been presented previously.[25] Sabadie[41] found an intermediate compound of the same molecular weight as (**7**), interpreting the structure as a guanidine (found in soil, Section 3.2.1), but likewise concluded that it was ultimately hydrolysed to form the chlorobenzenesulfonamide (**2**). Recent work on the hydrolysis of prosulfuron, a sulfonylurea closely related to chlorsulfuron, with a trifluoropropyl instead of chloro substituent on the benzene ring, has confirmed that the structure following the triazine ring opening of the *O*-desmethyl form of the sulfonylurea is the triuret by comparing the spectral data with those of a synthesized reference standard.[40,42] Levels of (**6**) reached a maximum of 13 and 14% for both radiolabels in our study (Fig. 2), similar to those (13·9 and 15·4%) of the same degradation product found in the prosulfuron hydrolysis study.[40] However, in our study the maximum level of (**6**) was achieved later (at 21 days) than in the prosulfuron study (7–10 days). In both experiments the maximum level of (**5**) (9% in our study) was reached at the end of the experiment (30–31 days) and a decline in (**6**) was followed by an increase in (**7**), suggesting that (**7**) forms from (**6**).

An average of 2 and 3% degradation of [^{14}C]chlorsulfuron (averaged for both radiolabels) was observed in buffer solutions at 25°C of pH 7 and pH 9, respectively, over the course of the 31-day experiment; this corresponded to pseudo-first-order hydrolysis half-lives of >365 days. The amounts degraded at these higher pH levels were significantly less than at pH 5 and not statistically different from 0 (at 0·01 level of confidence). Chlorsulfuron, with a pK_a of 3·6 (Table 1) is hydrolysed significantly faster at pH 5 than at higher pH levels because the anionic species (which is the predominant form in alkaline solutions) is much less susceptible to hydrolytic attack than the neutral species[5,8] and because the concentration of hydronium ions is much higher in more acidic solutions. At pH 5, the concentration of the neutral species is 100 times that at pH 7 (likewise for the hydronium ion concentration), resulting in faster acid hydrolysis. In work that may have a bearing on chlorsulfuron dissipation in alkaline soils, Huang and Stone[43] have found that the chlorsulfuron hydrolysis rate in neutral to alkaline solutions could be increased up to 100-fold by the addition of Zn^{2+}. Cu^{2+} also appeared to increase the hydrolysis rate, but less significantly than Zn^{2+}. It is unknown whether the Zn or Cu found in soils could affect hydrolysis.

3.1.2 *Direct aqueous photolysis*

When aqueous chlorsulfuron solutions buffered at pH 7 and 9 were irradiated at 25°C for 31 days (Section 2.2), 95–98% was recovered intact (Table 3). In non-irradiated vessels, 96–99% chlorsulfuron was recovered intact. When this experiment was conducted in solutions buffered at pH 5, only 39–40% of the chlorsulfuron was recovered intact in the non-irradiated samples after 31 days, and significantly less ($P \geqq 0{\cdot}01$) chlorsulfuron (29–33%) was recovered in the irradiated samples.

TABLE 3
Photolysis of Chlorsulfuron in Aqueous Buffers Exposed to Natural Sunlight for 31 Days in Wilmington, Delaware

	Radioactivity recovered as chlorsulfuron (%)							
	[*Phenyl-U-*^{14}*C*] *Chlorsulfuron*			[*Triazine-2-*^{14}*C*] *Chlorsulfuron*				
	Buffer pH			*Buffer pH*			*Cumulative radiation* (*watt* h^{-1} m^{-2})	
	5	*7*	*9*	*5*	*7*	*9*	*UV*	*Total*
Irradiated	29	97	97	33	98	95	~8000	~170 000
Non-irradiated	39	99	96	41	97	98	0	0
Difference	10	2	−1	7	−1	3		

The difference in recovery between non-irradiated and irradiated samples (7–10%) is assumed to equal the amount of photolysis corrected for aqueous hydrolysis. At pH 5 photolysis, corrected for hydrolysis (half-life 204 days), was approximately 8-fold slower than aqueous hydrolysis (half-life 26 days). Although direct photolysis can apparently contribute to overall degradation in acidic systems, hydrolysis most likely remains the major degradation mechanism operative for aqueous solutions. The degradation products formed in this experiment were similar to those in the aqueous hydrolysis experiment.

3.1.3 Soil surface photolysis

Evidence of the role that photolysis can potentially play in degradation of chlorsulfuron was observed in the soil surface photolysis study (Section 2.3). After 31 days of daily irradiation, 68% of the chlorsulfuron remained intact in the irradiated soil versus 86% in the dark control plates (Fig. 3a). The difference between the non-irradiated and irradiated treatments (18%) is assumed to represent the degradation due to soil surface photolysis, corrected for soil hydrolysis. The half-life in the irradiated soil (50 days) was much shorter than that in the non-irradiated soil (130 days). The difference of 80 days between the two values approximates to the soil surface photolysis half-life corrected for soil aqueous hydrolysis.

The major degradation products from [*phenyl-U*-^{14}C]chlorsulfuron in the irradiated soil were chlorobenzenesulfonamide (**2**) and *O*-desmethylchlorsulfuron (**6**). Neither was detected at levels $> 4\%$ of applied radioactivity at any sampling. Both of these degradation products were found in the dark controls, albeit at lower levels. Total recovery of radioactivity from irradiated plates treated with [*phenyl-U*-^{14}C]chlorsulfuron averaged 100·1($\pm$1·9)% over all samples, with 76·9, 8·7 and 8·0% represented by soil-extractable, soil-bound and [^{14}C]carbon dioxide fractions respectively. The major degradation products from [*triazine*-2-^{14}C]chlorsulfuron were triazine amine (**3**), *O*-desmethylchlorsulfuron (**6**) and triazine urea ((4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea; **8**). Only (**8**) was not seen in the dark controls, suggesting that the presence of this degradation product indicates a light-mediated dissipation mechanism. The level of (**8**) found reached a maximum of 7·0% of applied radioactivity, highest at the last sampling, and was higher than the level of (**6**), which reached 5·1% of applied radioactivity at the last sampling (Fig. 3b). It is postulated that (**8**) is further degraded to (**3**) through deamination (Fig. 1). Two other unidentified degradation products were present at levels $<2\%$ of the applied radioactivity. Total recovery of radioactivity from irradiated plates treated with [*triazine*-2-^{14}C]chlorsulfuron averaged 100·8($\pm$2·2)% over all samples, with 96·4, 3·6 and $<0{\cdot}9\%$ represented by soil-extractable, soil-bound and [^{14}C]carbon dioxide fractions, respectively. In a similar study with the sulfonylurea chlorimuron ethyl, the comparable pyrimidine urea was found to be a minor degradation product,[44] showing that formation of the heterocyclic urea under influence of light may not be unique to chlorsulfuron.

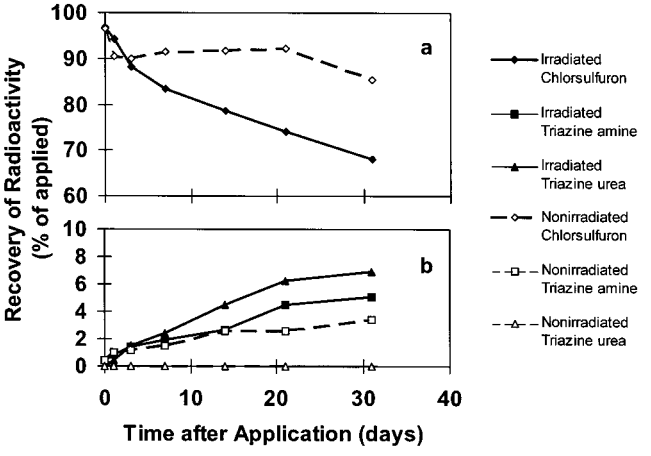

Fig. 3. Dissipation of 1·7 μg cm^{-2} [^{14}C]chlorsulfuron from the surface of a Nora silty clay loam soil (pH 8·0, 2·0% OM) at 25°C irradiated with light. (a) Dissipation of [^{14}C]chlorsulfuron (results averaged for both radiolabels) and (b) formation of selected degradation products from [*triazine*-2-^{14}C]chlorsulfuron.

Chlorsulfuron photolysis (corrected for hydrolysis) on the surface of this alkaline soil of pH 8·0 (half-life 80 days) was faster than aqueous photolysis (also corrected for aqueous hydrolysis) at pH 5 (half-life 198 days) and much faster than aqueous hydrolysis at pH 7 (half-life >365 days). It appears that the degradation rate on the soil surface exposed to light may have been faster than can be attributed to the rates of aqueous hydrolysis or direct aqueous photolysis, which suggests that the soil matrix, in combination with light, may be contributing more than indicated by either of these individual mechanisms. Direct photolysis on soil is assumed to be operable only on or within 0·1–0·5 mm of the surface,[45] and thus its potential contribution as a dissipation mechanism in the environment is limited once a precipitation event has washed chlorsulfuron into the soil. However, the upward movement of chlorsulfuron with capillary rise of the water front to the surface, demonstrated in soil columns,[19,46] could occur in the field under conditions of net negative water balance and may parallel the demonstrated accumulation of relatively mobile salts on the surface seen in soils of arid regions.[47] It is reasonable to believe that this type of transport could occur with chlorsulfuron in arid regions during late spring and summer, resulting in a zone of accumulation of chlorsulfuron at the soil–atmosphere interface. The contribution of soil surface photolysis (or perhaps indirect photolysis) to the overall dissipation of chlorsulfuron in arid, sunny climates is not understood and has perhaps been underestimated,[45] particularly in alkaline soils where hydrolysis rates are curtailed. These concepts need further investigation in order to ascertain

their relative importance. Relative to other processes, i.e. aqueous hydrolysis, the contribution of photolysis (whether direct or indirect) to overall dissipation in acidic soils is expected to be minor. It can be speculated that direct photolysis of chlorsulfuron remaining on plant surfaces may also occur, but no evidence of this at present exists.

3.2 Aerobic and anaerobic soil metabolism

3.2.1 Aerobic soil metabolism studies

In a laboratory experiment (Section 2.4.1.) [*phenyl-U*-^{14}C]- and [*triazine*-2-^{14}C]chlorsulfuron applied to a Keyport silt loam soil degraded quickly (Fig. 4), following a biexponential, or two-stage, decline curve with an initial pseudo-first-order half-life (averaged for both radiolabels) of 20 days (0–60 days) and 128 days for the second stage of slower decline (60–180 days). This deviation of soil degradation kinetics from first-order kinetics and exhibition of biexponential, or two-stage, degradation kinetics, has been observed for chlorsulfuron and was partly explained through the decrease of availability of chlorsulfuron to soil microbes through adsorption[48] or movement to a protected compartment.[49,50] Another partial explanation for this phenomenon could be that a decline in microbial viability, observed in long-term soil metabolism studies conducted in glass vessels in the laboratory,[51] may have contributed to the decrease in degradation rate. During the slower decline stage, chemical hydrolysis of chlorsulfuron in the protected compartment continues at a slower rate than microbial degradation, which results in an overall slower degradation rate.[50] Both microbial and aqueous hydrolysis degradation are responsible for

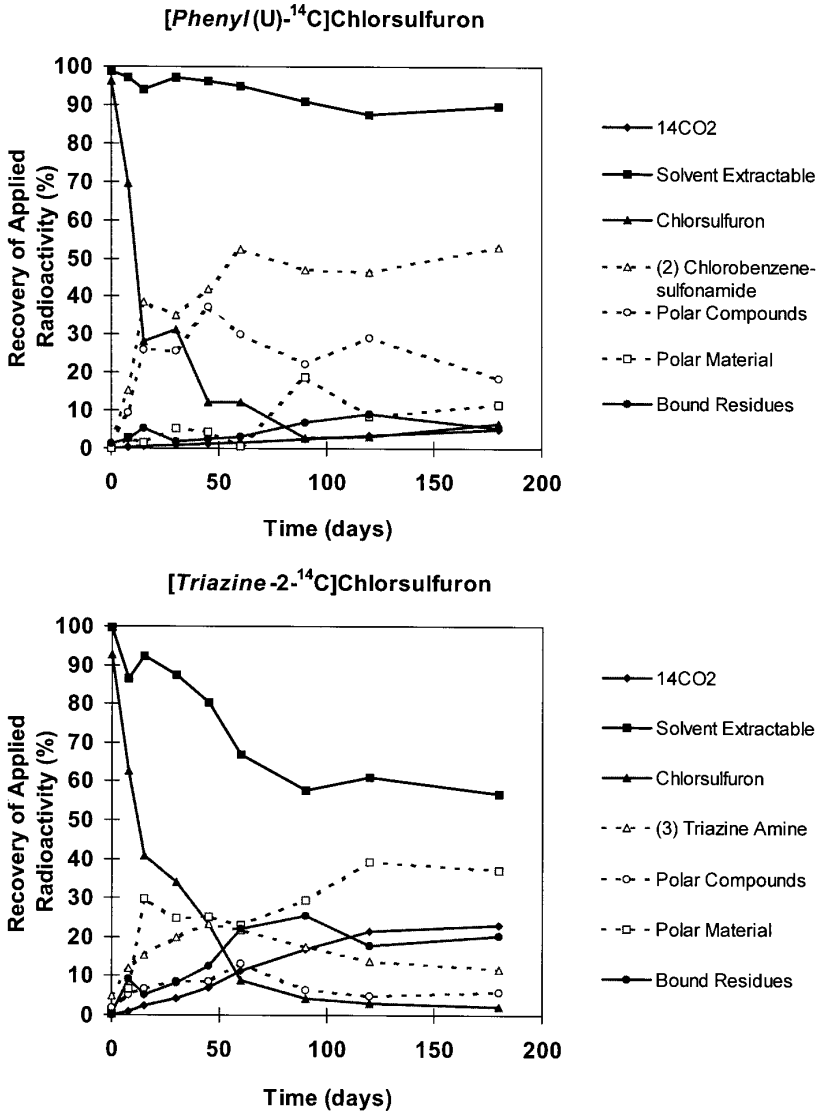

Fig. 4. Degradation of 0·1 mg kg^{-1} [*phenyl-U*-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C]chlorsulfuron and formation of key degradation products in a Keyport silt loam soil at 25°C. (Solvent-extractable component is the sum of chlorsulfuron and components listed with dashed lines; polar compounds identified as *O*-desmethylchlorsulfuron (**6**), hydroxy triazine amine (**10**), dihydroxy triazine (**5**), 5-hydroxy chlorsulfuron (**11**), ring-opened carbamoyl guanidine (**9**).

chlorsulfuron dissipation; the relative importance of each has been addressed previously[52–54] and will not be discussed in detail here.

At the end of 180 days, nearly 90% of the radioactivity initially applied as [*phenyl-U*-^{14}C]chlorsulfuron could be extracted from the soil, of which the majority (52% of applied) was chlorobenzenesulfonamide (**2**). It formed quickly, accounting for approximately half of the applied radioactivity by the 60-day sampling. Other components of the solvent-extractable residues were polar compounds, comprising 19% of initial radioactivity and were identified by TLC and GC/MS analysis as *O*-desmethylchlorsulfuron (**6**), hydroxy triazine amine (4-amino-6-methyl-1,3,5-triazin-2-ol; **10**) dihydroxy triazine (**5**), 5-hydroxy chlorsulfuron (1-(2-chloro-5-hydroxyphenylsulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea; **11**), and a fifth degradation product identified as ring-opened carbamoyl guanidine (1-(2-chlorophenylsulfonyl)-3-(ureido-imino)urea, **9**). The latter compound is different from ring-opened acetyltriuret (**7**; Fig. 1) found in the aqueous hydrolysis study (Section 3.1.1). The unidentified polar materials accounted for 12% of the applied radioactivity and perhaps consisted of *phenyl*-ring fragments incorporated into the soil organic matter (OM) because they could only be removed from soil by caustic hydrolysis. Intact chlorsulfuron accounted for 7% of the applied radioactivity. Both the identified and unidentified polar compounds showed initial increases and then declined during the course of the 180-day study. Bound residues and [^{14}C]carbon dioxide evolution each accounted for approximately 5% of initially applied radioactivity.

When the initial radioactivity was applied as [*triazine*-2-^{14}C]chlorsulfuron, nearly 60% could be extracted after 180 days, considerably less than from the [*phenyl-U*-^{14}C]chlorsulfuron treatment. The major component of the solvent-extractable residues for this radiolabel was the polar material, accounting for nearly 40% of applied radioactivity and similar in makeup to those from the [*phenyl-U*-^{14}C] radiolabel. Triazine amine (**3**) comprised a further 12%, unspecified polar compounds and chlorsulfuron comprised a further 6% and 2%, respectively, of the initially applied radioactivity. The triazine amine (**3**) reached a maximum of nearly 25% of applied radioactivity at the 45-day sampling before declining to less than half that at the 180-day sampling. Bound residues (20%) and [^{14}C]carbon dioxide evolution (23%) were much higher for the [*triazine*-2-^{14}C]chlorsulfuron than for the [*phenyl-U*-^{14}C]chlorsulfuron, suggesting that the triazine moiety is more susceptible to microbial attack than the chlorobenzenesulfonamide moiety. In an identical experiment conducted with [*triazine*-2-^{14}C]chlorsulfuron using autoclave-sterilized soil, the bound residues at the end of 180 days accounted for only 3% and [^{14}C]carbon dioxide evolution only 2% of the initial radioactivity (data not shown), illustrating the important contribution of microbial processes to the overall degradation and formation of bound residues. The formation of polar material, bound residues, and [^{14}C]carbon dioxide from both radiolabeled chlorsulfuron treatments appeared to plateau by the end of 180 days, indicating a slowdown in the rate of degradation and mineralization of degradation products by microbes, following two-stage degradation kinetics similar to chlorsulfuron. As in the aqueous hydrolysis studies, the chlorobenzenesulfonamide (**2**) and triazine amine (**3**) appeared to be the major metabolites of aerobic soil dissipation, also found in a study by Marucchini *et al.*[55] and implied by Iivanainen and Heinonen-Tanski.[17]

Because many triazine herbicides are considered persistent in soil as judged by their average soil half-lives,[56] a long-term degradation experiment (Section 2.4.2) was conducted with radiolabeled (**3**) ([2-^{14}C]4-methoxy-6-methyl-1,3,5-triazin-2-amine), applied at 0·1 mg kg^{-1} in a Keyport silt loam soil (pH_{water} 4·3). Results showed that the triazine amine degraded throughout the 475-day period, but with the rate slowing after 180 days (Fig. 5). It is conceivable that the microbial population was severely stressed during the extremely long experimental period, and that during the latter stage microbial degradation was no longer optimal, although [^{14}C]carbon dioxide continued to evolve and the bound fraction continued to increase at a slower rate after the 100-day sampling. Two-stage degradation kinetics similar to those for chlorsulfuron are presumed to have been operable, since it was demonstrated that micro-organisms were in part responsible for degradation of (**3**). It is not known whether (**3**) is subject to hydrolytic degradation, but this is not predicted to be significant at pH levels found in normal agronomic soils (Zimmerman, W. T., DuPont Company, 1997 pers. commun.). The first stage of degradation (half-life over the first 180 days = 166 days) was considerably slower than that for the parent chlorsulfuron (**1**), (half-life 20 days). The half-life calculated for (**3**) in the chlorsulfuron soil metabolism study (by simply taking time points without considering the rate of formation) was 128 days. If its rate of formation is taken into account, it is likely to be shorter. The particular batch of Keyport soil used for this study was more acidic than that used in the aerobic soil metabolism study (pH 4·3 versus 6·4), which may have affected the degradation rate because of the effect of pH on the microbial composition or activity (not measured). The consequence of pH itself on the chemical degradation of the triazine amine is unknown. However, in this study [^{14}C]carbon dioxide evolved continuously and bound residues formed continuously, albeit considerably more slowly after the 100-day sampling, which suggested that triazine amine degradation and subsequent incorporation into bound fractions would continue. Major degradation products were the hydroxy triazine amine (**10**) dihydroxy triazine

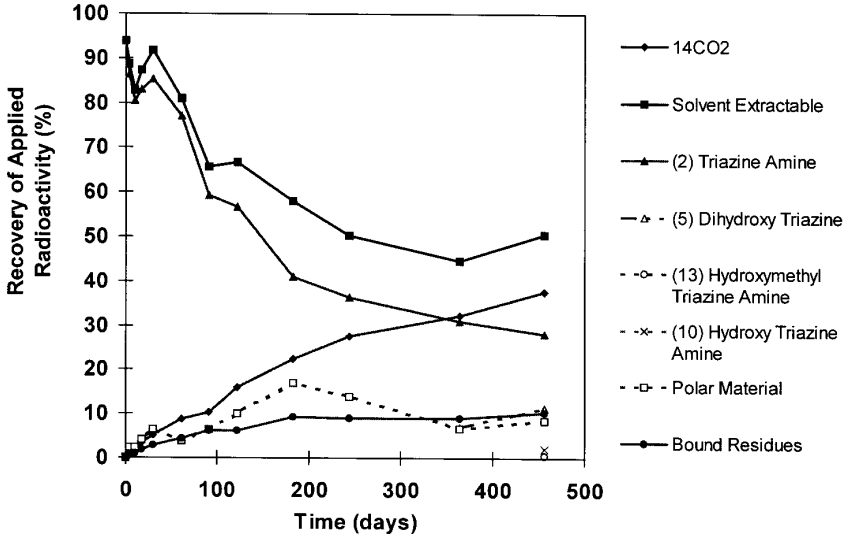

Fig. 5. Degradation of 0·1 mg kg^{-1} [2-^{14}C]4-methoxy-6-methyl-1,3,5-triazin-2-amine and formation of key degradation products in a Keyport silt loam soil at 25°C (Solvent-extractable component includes parent chlorsulfuron and components listed with dashed lines; polar compounds identified as *O*-desmethylchlorsulfuron (**6**), hydroxy triazine amine (**10**), dihydroxy triazine (**5**), 5-hydroxy chlorsulfuron (**11**), ring-opened carbamoyl guanidine (**9**).

amine (**5**) and the hydroxymethyl triazine amine (4-methoxy-6-methanol-1,3,5-triazin-2-methanol; **13**).

The proposed pathways for [^{14}C-]chlorsulfuron degradation in the soil environment under aerobic conditions are presented in Fig. 6. The major pathway is sulfonylurea bridge cleavage through aqueous hydrolysis, forming the chlorobenzenesulfonamide (**2**) and triazine amine (**3**). Subsequent *O*-demethylation of (**3**) and deamination yields dihydroxy triazine (**5**). These then undergo further degradation to yield carbon dioxide and fractions which are then incorporated into the soil OM. Another pathway begins with *O*-demethylation of the triazine moiety of chlorsulfuron, which then undergoes a rapid series of steps to yield ring-opened carbamoyl guanidine (**9**). In contrast to the ring-opening in aqueous solution (Fig. 1), the 1,6 bond of the triazine ring (denoted by an encircled '2' in Fig. 6) appears to cleave. Hydroxylation of the chlorobenzene moiety to yield 5-hydroxychlorsulfuron (**11**) appears to be a relatively minor pathway in aerobic soils, but is likely to be enzyme-mediated, since it is the primary step in the mechanism of chlorsulfuron tolerance by cereals.[57] It appears that chlorsulfuron degradation in soils occurs in two stages, and that more rapid microbially mediated processes dominate the first stage and the slower hydrolytic processes dominate the second stage.[50,52]

3.2.2 Effects on soil microbiological processes

The effect of chlorsulfuron on nitrification of ammonia in two soils over a 70-day period (Section 2.4.3.) is shown in Fig. 7. In both soils a stimulation of nitrification by chlorsulfuron was observed at both tested concentrations (average of 14% at 0·1 and 21% at 1·0 mg kg^{-1}, respectively). Although the overall magnitude of the effect was low, an analysis of variance showed that the stimulation by chlorsulfuron, as well as the difference between soils, was statistically significant ($P \leqq 0{\cdot}0001$). The 1·0 mg kg^{-1} concentration resulted in a slightly higher level of stimulation than the 0·1 mg kg^{-1} concentration. These results show that soil nitrification is not expected to be affected negatively by concentrations expected from normal chlorsulfuron applications, corroborating previous studies.[58–60] Effects of chlorsulfuron (at 1·0 mg kg^{-1}) on degradation of ^{14}C-cellulose over 60 days and ^{14}C-protein degradation over 30 days were minor (Table 4), showing slight overall stimulation (4%) and reduction (5%), respectively. Analysis of variance revealed that these treatment differences were statistically significant ($P \leqq 0{\cdot}0001$), but in absolute magnitude were small. The potential effects of the degradation products of chlorsul-

TABLE 4
Effect of Chlorsulfuron (1 mg kg^{-1}) on Degradation of ^{14}C-Cellulose for 60 Days and ^{14}C-Protein for 30 Days in Two Soils

Soil and treatment	*Amount of applied radioactivity recovered as $^{14}CO_2$ (%)*	
	^{14}C-Cellulose treatment	*^{14}C-Protein treatment*
Fallsington sandy loam control	50	31
Fallsington sandy loam treated	60	30
Keyport silt loam—control	37	30
Keyport silt loam—treated	29	29
Average—control	44	31
Average—treated	45	30

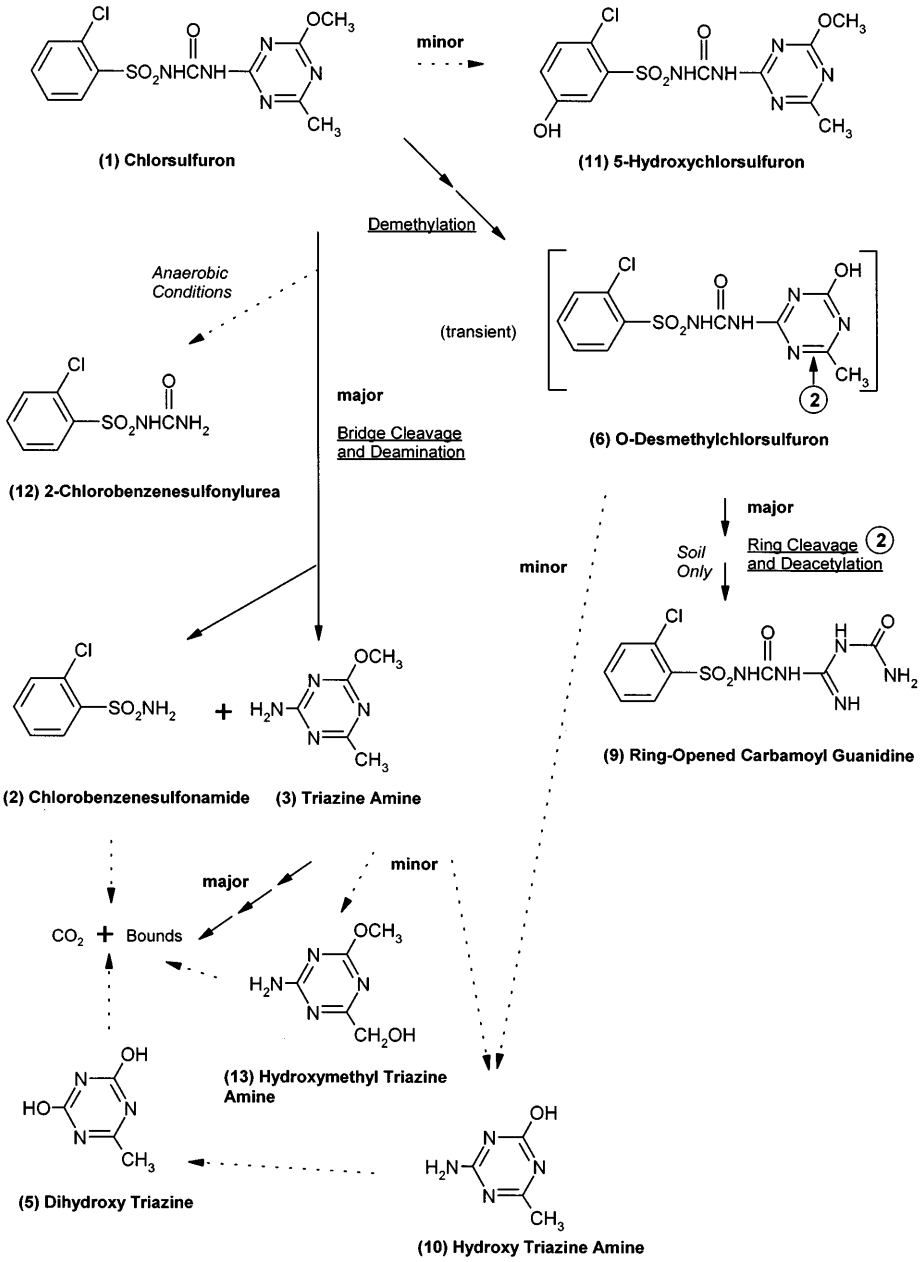

Fig. 6. Proposed degradation pathways of chlorsulfuron in soil under aerobic and anaerobic conditions.

furon upon soil microbial processes was not directly tested; however, because the experimental set-up was identical to the soil metabolism study and these experiments extended over a 30–70-day period, it can be assumed that soil microbes were exposed to significant levels of some of the degradation products seen in Fig. 4. Perucci *et al.*[61] found that chlorsulfuron at field rates (20 g AI ha^{-1}) moderately affected the biomass (SIR) and carbon dioxide evolution, but did not affect specific respiration of two Italian soils, from a permanent pasture and a forest, ostensibly not previously treated with pesticides.

Effects reported in the literature of chlorsulfuron on the growth and reproduction of other plant-associated, soil and benthic micro-organisms themselves are generally minor, or occurring at concentrations above those expected in soils[62,63] or natural waters.[64] Using an expected environmental concentration of 0·02 mg $litre^{-1}$ calculated by assuming an overspray of a 15-cm deep water body with 15 g AI ha^{-1} of chlorsulfuron, no significant inhibition of four species of algae and six species of cyanobacteria in pure cultures has been reported.[65] In a survey of plant-associated rhizobacteria, only two strains of *Azospirillum lipoferum* and one strain of *Pseudomonas luteola* out of 18 total strains were affected, inhibited by chlorsulfuron concentrations of 11·6 mg $litre^{-1}$.[66] At much higher concentrations of 1085 mg $litre^{-1}$, only two strains of *Azotobacter agilis* and a *Bacillus cereus* strain were affected in a test of 12 soil micro-organisms in pure culture.[67] Growth of a phototrophic bacterium *Rhodospirillium rubrum* was inhibited at concentrations above 0·004 mg $litre^{-1}$,[68]

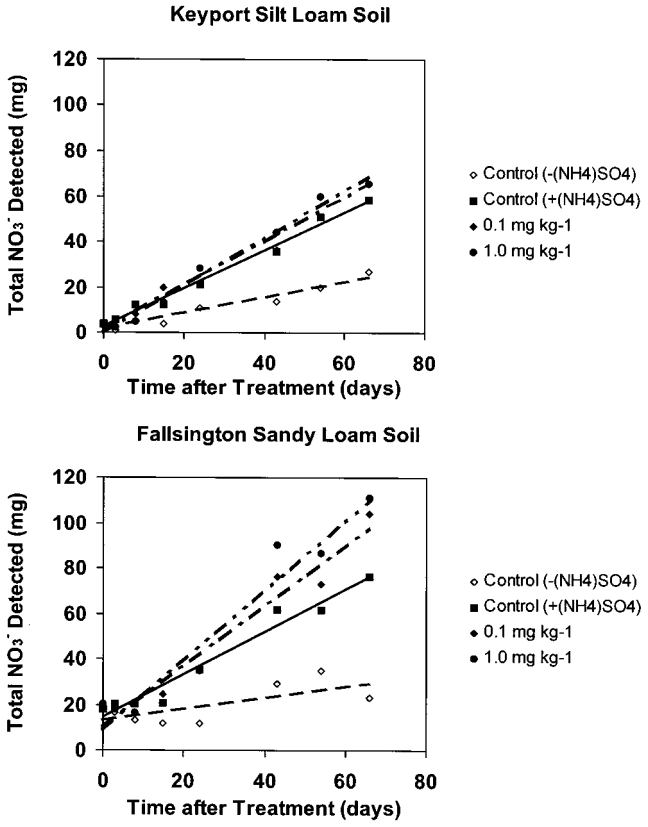

Fig. 7. Effect of chlorsulfuron on soil nitrification in two soils.

while growth of the fungal pathogen *Fusarium graminearum* Schwabe Group 1 was not inhibited at concentrations up to 0·05 mg litre^{-1}.[69] Effects of chlorsulfuron on growth of various *Rhizobium* species have been reported to be insignificant[70] to relatively moderate[71] at a concentration of 2 mg litre^{-1}.

When discussing potential effects of chlorsulfuron on soil microbes and processes, it is useful to calculate the expected concentrations in both the soil-adsorbed and soil-water fractions. Assuming that an entire application of Glean® 75 DF to cereals at a rate of 15 g AI ha^{-1} reaches the soil surface, the theoretical chlorsulfuron concentration in a soil of bulk density 1·5 g cm^{-3} with an even distribution to a depth of 1 mm is 1 mg kg^{-1}. The theoretical soil water concentration must account for the water content of the soil. Assuming that the range of volumetric water content found normally in soils immediately after application falls between 0·02 (permanent wilting point of a sandy soil) and 0·33 (field capacity of a silt loam soil),[72] and that the range of adsorption to soil falls between 10 and 50% (Table 5), the theoretical soil water concentration is calculated for the top 1 mm to range from 67·5 to 2·3 mg kg^{-1}. At a 1-cm depth, this range decreases to 6·75 to 0·23 mg kg^{-1} and at a 10-cm depth this decreases further to 0·675 to 0·023 mg kg^{-1}. This calculation has not factored in degradation of the chlorsulfuron molecule, which can occur rapidly in certain soils and would result in lower concentrations. Thus it is reasonable to assume that the 1 mg kg^{-1} concentration used in the experiments reported herein is within the range of the concentrations in the soil water in the top 10 cm of soil soon after application of a 15 g AI treatment of chlorsulfuron. This concentration would theoretically be exceeded greatly only at the surface of the soil (top 1 mm) immediately after application. Based upon the results of the studies reported herein and effects reported in the literature, the potential for adverse effects of chlorsulfuron and its degradation products on microbes and microbial processes is likely to be limited to short periods immediately after application when the chemical is concentrated at the soil surface.

3.2.3 *Anaerobic soil/aquatic sediment study*

A laboratory degradation experiment conducted in a non-sterile, sediment/water system (Section 2.5) treated with [*phenyl-U*-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C] chlorsulfuron demonstrated that as radioactivity (applied to water) decreased in the water fraction, distribution into the sediment fraction subsequently increased for both radiolabeled compounds (Fig. 8). However, a large proportion of applied radioactivity (>70%) still remained in the water fraction one year after treatment. The major initial degradation product found in the combined sediment/water system (Fig. 9) from [*phenyl-U*-^{14}C]chlorsulfuron detected at 7 days (at 3%) was 2-chlorobenzenesulfonylurea (**12**), unique to this environment. The remainder of the degradation products were similar to those in the aqueous hydrolysis experiment (Sect. 3.1.1). At the end of the experiment (70 days), the chlorobenzenesulfonamide (**2**) accounted for 14%, polar compounds (identified by TLC analysis and mass spectrometry as primarily *O*-desmethylchlorsulfuron (**6**) and ring-opened acetyltriuret (**7**)) accounted for 11%, bound residues

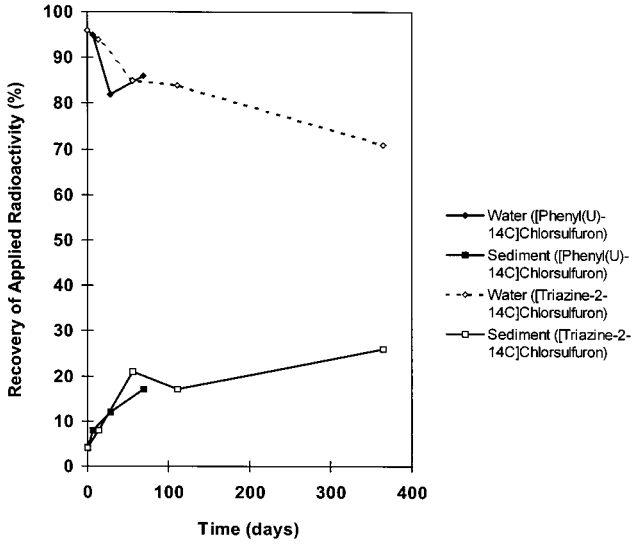

Fig. 8. Distribution of radioactivity of [*phenyl-U*-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C] in nonsterile flooded sediment water system at 25°C with time.

TABLE 5

Adsorption and Desorption Constants[a] for Chlorsulfuron and Mobility Classification Based on Soil Thin-Layer Chromatography for Chlorsulfuron, and its Degradation Products Chlorobenzenesulfonamide and Triazine Amine on Four Soils

	Adsorption						*Desorption*			*Mobility classification*[c]		
Soil	K_{ads}	K_{OM}	K_{OC}	K_{fads}	*1/n*	*Amt %*[b]	K_{des}	K_{OM}	K_{OC}	*Chlorsulfuron*	*Chlorobenzene-sulfonamide*	*Triazine amine*
Woodstown sandy loam	0·08	7	13	0·09	0·85	8·3	0·31	30	52	4	4	3
Madera loam	0·27	31	54	0·28	0·90	22·3	0·10	12	20	4	4	1
Keyport silt loam	0·33	17	30	0·38	0·88	28·6	0·36	19	33	3	3	1
Flanagan silt loam	0·85	20	34	0·91	0·91	49·0	1·01	23	40	3	3	1
Average	0·38	19	33	0·42	0·89	27·1	0·45	21	36			

[a] K_{ads} : Linear Adsorption Coefficient, K_{des} Linear Desorption Coefficient, K_{fads} : Freundlich Adsorption Coefficient

[b] Amount adsorbed as a percentage of total amount [^{14}C]chlorsulfuron in initial solution averaged over entire concentration range

[c] Based upon the classification scheme of Helling (1 = immobile, 2 = low mobility, 3 = moderate mobility, 4 = highly mobile, 5 = very highly mobile).[80]

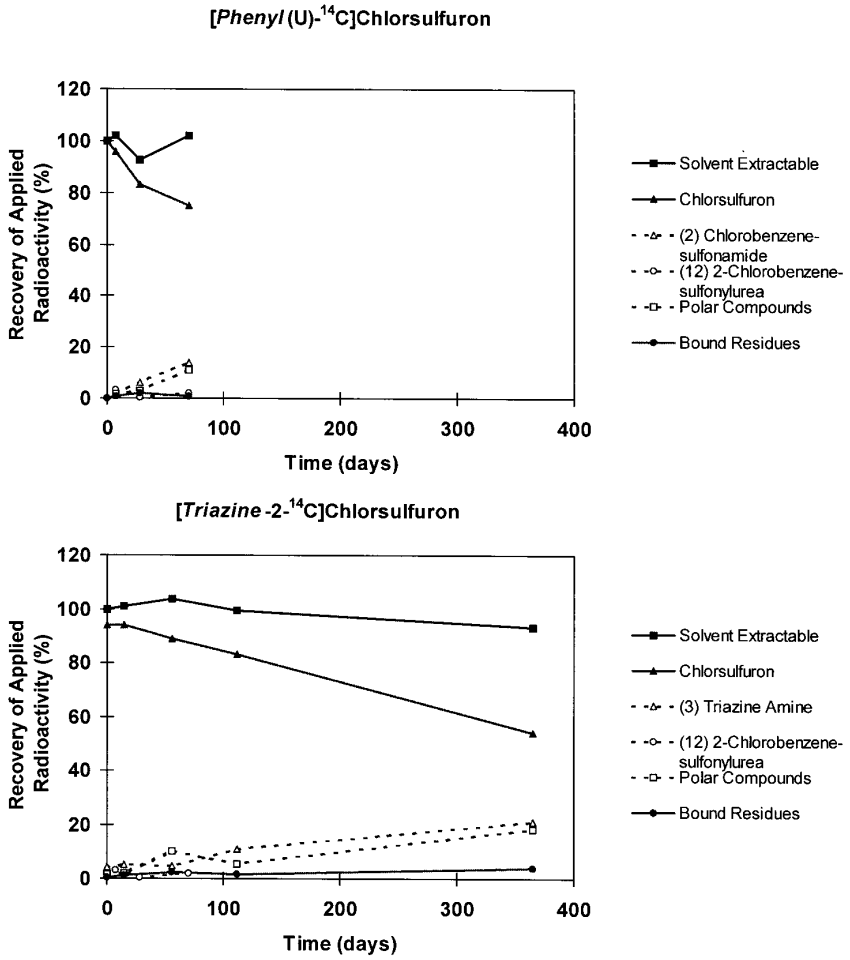

Fig. 9. Degradation of [*phenyl-U*-^{14}C]chlorsulfuron and [*triazine*-2-^{14}C]chlorsulfuron and formation of key degradation products in a nonsterile, flooded sediment/water system at 25°C. Polar compounds identified as *O*-desmethylchlorsulfuron (**6**), hydroxy triazine amine (**10**), dihydroxy triazine (**5**), 5-hydroxy chlorsulfuron (**11**), ring-opened carbamoyl guanidine (**9**).

accounted for 1% and intact chlorsulfuron accounted for 75% of applied radioactivity. In other studies conducted with different sediments under the same conditions, (**9**) rather than (**7**) appeared to accumulate (data not shown). In the sterile system, 66% of the applied radioactivity was recovered as intact chlorsulfuron after 70 days (data not shown).

The degradation of [*triazine*-2-^{14}C]chlorsulfuron was followed over a much longer period of 365 days (Fig. 9). Major degradation products at the end of the study in the combined sediment/water system were the triazine amine (**3**) (21%) and polar compounds (18%, also identified by TLC analysis and mass spectrometry as primarily) *O*-desmethylchlorsulfuron (**6**) and ring-opened carbamoyl guanidine (**9**)), with lesser amounts of bound residues (3·7%) found. Intact chlorsulfuron accounted for 54% of the applied radioactivity in the nonsterile system and 37% in the sterile system (data not shown). The reason for finding less intact chlorsulfuron in sterile treatments than in the microbially active treatments is likely to be greater hydrolysis through the use of sodium azide to sterilize the systems, which lowered the pH (initial pH 6·7, final pH 7·4 in non-sterile water versus initial pH 6·1, final pH 6·3 in sterile water). The tendency for [*triazine*-2-^{14}C]chlorsulfuron to degrade more completely and form higher amounts of degradation products in the non-sterile system than in the sterile system reinforces the theory that the triazine moiety is susceptible to microbial attack, suggested by the aerobic soil study (Section 3.2.1).

The rate of chlorsulfuron degradation was much slower under flooded, anaerobic conditions (half-life >365 days) than in the aerobic soil metabolism study (Section 3.2.1) which used a soil with similar characteristics (half-life 20 days). Aqueous hydrolysis in the water phase is likely to have been the primary dissipation mechanism, indicated by the long chlorsulfuron half-life (similar to that in pH 7 water). Berger and Wolfe[37] found much faster dissipation in two sediments, with half-lives of 88 and 182 days at 25°C under non-sterile conditions and 301 and 102 days under sterile conditions, than in our studies. Potentially slower than aerobic soil metabolism, anaerobic soil metabolism is expected to be a relatively unimportant dissipation pathway for chlorsulfuron in the environment because levels reaching groundwater are expected to be low,

TABLE 6
Selected Toxicological Properties of Chlorsulfuron and its Major Soil Degradation products Chlorobenzenesulfonamide and Triazine Amine

Toxicological property	*Chlorsulfuron*[a]	*Chlorobenzenesulfonamide*	*Triazine amine*
Oral LD_{50} (male rat)	5545 mg kg^{-1}	—	1680 mg kg^{-1}
ALD[b] (male rat)	—	7500 mg kg^{-1}	—
Skin sensitization (guinea pig)	Negative	Negative	Negative
Skin irritation (guinea pig)	Negative	Mild; reversible	Mild to none
Eye irradiation (rabbit)	Mild; reversible	Negative	Mild[c], reversible
Mutagenicity	Negative[d]	Negative[e]	Negative[e]

[a] For a more complete listing for chlorsulfuron see reference 4.
[b] Approximate Lethal Dose: lowest oral dose causing mortality within 14-day recovery period.
[c] Slight, reversible corneal opacity.
[d] Battery of five assays including Ames *Salmonella typhimurium*, Rat Dominant Lethal, Chinese Hamster Ovary, *in vivo* Cytogenetic and DNA Repair (UDS Liver Hepatocyte).
[e] Ames *Salmonella typhimurium*.[14]

estimated to be below 0·000 01 mg $litre^{-1}$ for a soil moderately vulnerable to leaching.[73] Experimenters conducting run-off experiments with chlorsulfuron[74] and sulfometuron,[75,76] a less soil-mobile sulfonylurea, concluded that run-off resulted in losses which reached a few percent of applied amounts under simulated worst-case conditions. In Swedish lysimeter experiments, a maximum 0·6% and 0·06% of chlorsulfuron applied at 8 g AI ha^{-1} (double the labeled use rate) was detected leaching to a depth of 1·18 m (bottom of lysimeter) in vulnerable, sandy soils, with concentrations measured up to 0·000 043 mg $litre^{-1}$.[77,78] It was concluded that amounts of chlorsulfuron expected to reach stream water would not reach biological effect concentrations. This assessment is partially contradicted by the results of a study in Norway where up to 2% of applied chlorsulfuron was found in the sub-surface drainage water running off a field with 4–8·5% slopes and collected at some distance from the treated area.[79] Much less chlorsulfuron was found in the surface runoff (<0·5% of applied), agreeing with the previously cited work. However, this particular study was conducted at a site at which major modifications of topography and soil structure had been conducted, making it difficult to extrapolate these findings to normal agronomic soils.

3.2.4 Toxicity of major degradation products

Selected acute toxicological properties of the chlorobenzenesulfonamide (**2**) and triazine amine (**3**) are contrasted versus those for chlorsulfuron in Table 6. They indicate the minimal risk of acute toxicity from these major degradation products of chlorsulfuron, similar to that for chlorsulfuron itself. Results of a glasshouse screening test (Section 2.9) showed that neither pre- or post-emergent applications of 2000 g AI ha^{-1} adversely affected any of the tested plant species, with no observable injury symptoms detected (data not shown).

3.3 Laboratory soil mobility studies

3.3.1 Adsorption desorption

In a 1 : 1 soil : solution batch equilibrium study (Section 2.6) with [*phenyl-U*-^{14}C]chlorsulfuron on four soils, K_{ads} values of 0·08 to 0·85 and K_{oc} values of 13 to 54 were calculated (Table 5). From these results, adsorption could be described as very low. Average amounts of chlorsulfuron adsorbed to the soil (in % of the total amount added to the 1 : 1 soil : solution system) ranged from 8·3% on the Woodstown sandy loam to 49% on the Flanagan silt loam. Desorption could be described as moderate, with K_{des} values ranging from 0·1 to 10 and K_{oc} values ranging from 20 to 52.

3.3.2 Soil thin-layer chromatography

Soil thin-layer chromatography (Section 2.7) results compared the relative mobility potential of chlorsulfuron and its major soil degradation products chlorobenzenesulfonamide (**2**) and triazine amine (**3**) (Fig. 10). The R_f values for chlorsulfuron on these soils have previously been published.[4,8] The chlorobenzenesulfonamide (**2**) (average $R_f = 0·57$) was slightly less mobile

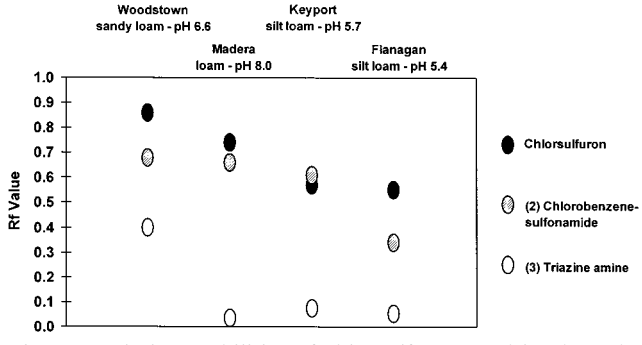

Fig. 10. Relative mobilities of chlorsulfuron, and its degradation products chlorobenzenesulfonamide and triazine amine based upon soil thin-layer chromatography.

than chlorsulfuron (average $R_f = 0{\cdot}68$), though the difference was not significant in a T-test of least squares means ($P = 0{\cdot}01$), and could be classified as moderately to highly mobile, Classes 3 and 4 (Table 5), respectively, in Helling's classification scheme.[80] The triazine amine (**3**) (average $R_f = 0{\cdot}14$) was much less mobile than chlorsulfuron and was classified as relatively immobile (Class 1) in all but the Woodstown sandy loam, where it could be classified as moderately mobile (Class 3). This differs from the assessment of triazine amine degradation products of sulfonylureas as probable leachers by Barrett.[81] The highest chlorsulfuron mobility was observed in the Woodstown sandy loam, which had the lowest OM content ($R_f = 0{\cdot}86$) and the lowest mobility was observed in the Flanagan silt loam ($R_f = 0{\cdot}55$), which had the highest OM content (and also the lowest pH). Unexpectedly, R_f values corresponded highest with sand content ($R^2 = 0{\cdot}96$) and less with OM content ($R^2 = -0{\cdot}74$) or soil pH ($R^2 = 0{\cdot}66$). The highest correlation of the mobility of the two major degradation products with a soil property was the correlation of the R_f of (**2**) with OM content ($R^2 = 0{\cdot}99$). The results suggest that the chlorobenzenesulfonamide (**2**) and the triazine amine (**3**) will have slightly less and much less soil mobility potential, respectively, than chlorsulfuron.

3.3.3 *Column leaching*

Column studies (Section 2.8) conducted using the conventional method of treating pre-wet, saturated columns have demonstrated that chlorsulfuron is highly mobile under these simulated worst-case conditions.[12,46] Comparable behavior was demonstrated in this study conducted with a protocol similar to those used in the previously cited studies. When [*phenyl-U*-^{14}C]chlorsulfuron was applied to the surface of the pre-wet columns (46 cm depth, 5 cm diameter) of Fallsington sandy loam (pH_{water} 5·6, OM 1·4%) and Flanagan silt loam (pH_{water} 6·4, OM 4·0%), followed by immediate initiation of water percolation, the columns retained 9% and 8%, respectively, of initially applied radioactivity (Fig. 11—'Fresh' treatment). However, for samples in which the chlorsulfuron was applied to soil and aged for 30 days in a greenhouse prior to placement on top of the columns and initiation of water percolation (Fig. 11—'Aged' treatment), the mobility was much less, with 88 and 72%, respectively, of applied radioactivity retained in the soil columns. Additionally, a greater percentage of the total radioactivity remained closer to the soil surface in the 'Aged' treatment than in the 'Fresh' treatment.

Characterization of the leachate from the Fallsington sandy loam by TLC analysis showed that 46% of the total radioactivity was attributable to intact chlorsulfuron, 24% to chlorobenzenesulfonamide (**2**), and the remainder to unidentified polar compounds. These results demonstrate that chlorsulfuron degraded during the course of the 30-day aging period in the soils

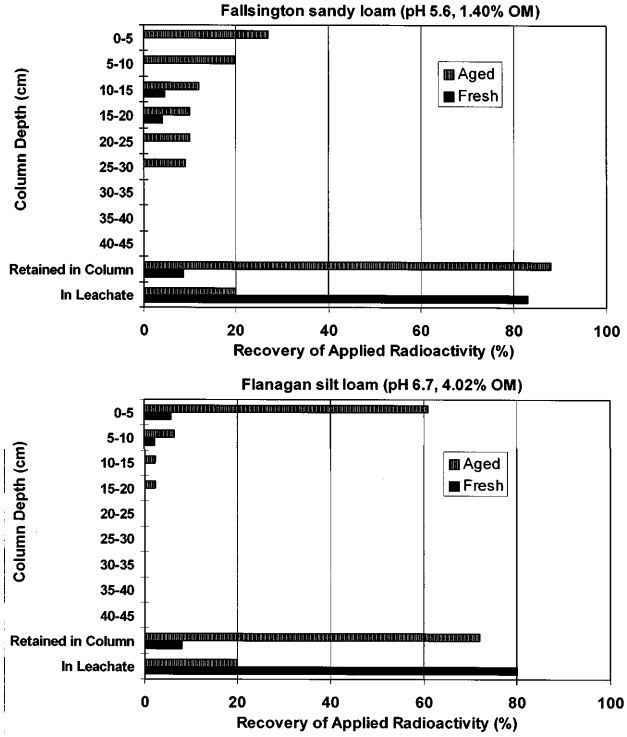

Fig. 11. Soil column leaching studies in two soils with chlorsulfuron following percolation of 508 mm water immediately ('Fresh') or after an aging period of 30 days in a greenhouse ('Aged').

(maintained at 75% of moisture-holding capacity) and that, at the initiation of leaching, only a portion of the radioactivity represented intact chlorsulfuron. No characterization of the radioactivity was conducted for the leachate from the Flanagan silt loam or for that remaining in the column for either soil. Total recovery of radioactivity from all columns (including soil extracts, soil combustions and leachate) ranged from 88 to 108%, demonstrating that potentially little volatilization or other type of loss had occurred. The decreased mobility of some of the major degradation products (demonstrated in the soil TLC study) and integration of residues into the soil matrix during the aging period are likely to have contributed to the decreased overall mobility of the total applied radioactivity through the column in the aged treatment. Column leaching studies conducted with aged herbicide residues are considered to be more representative of a typical field scenario than unaged column leaching studies where herbicide is applied to a pre-wet column and followed immediately by infiltration under near-saturated conditions.[82] The deficiencies of batch equilibrium and saturated column studies in providing accurate mobility assessments for the surface layer of soil have been previously noted.[83]

4 CONCLUSIONS

These studies indicate that chlorsulfuron degrades through several mechanisms both hydrolytically in

aqueous solution and microbially in soil to form a variety of degradation products in soil (and water), which ultimately degrade further to form carbon dioxide and fragments that are incorporated into the soil matrix. The chlorsulfuron molecule presents a number of initial points of attack which differ according to the particular degradation pathway. Cleavage of the sulfonylurea bridge is a major pathway occurring in water and soil and results in formation of the major degradation products chlorobenzenesulfonamide (**2**) and triazine amine (**3**). These two degradation products demonstrated a lack of phytotoxicity to all tested crops and weeds when evaluated in a glasshouse screen and also exhibited low acute toxicity to animals (Table 6). Although triazine herbicides are considered persistent in soils, the triazine moiety of chlorsulfuron appears to be more susceptible to microbial attack than the chlorobenzenesulfonamide moiety and appears to break apart by at least two different mechanisms. The triazine ring was cleaved at either the 1,2 position, which occurred in aqueous solution and soil, or at the 1,6 position, which occurred only in soil. Aqueous photolysis seems to be a relatively insignificant degradation pathway for chlorsulfuron, especially compared with aqueous hydrolysis. The soil photolysis study resulted in faster degradation of chlorsulfuron than could be explained by aqueous photolysis alone, indicating that perhaps an indirect photolysis mechanism could contribute to overall degradation. Formation of triazine urea (**8**), found only in the irradiated treatment of the soil surface photolysis study, appears to be uniquely related to the presence of light and soil and suggests the presence of a light-mediated reaction. Degradation in nonsterile, anaerobic, flooded systems proceeded more slowly than in aerobic soil systems and resulted in formation of another unique degradation product, 2-chlorobenzenesulfonylurea (**12**), which was not detected under aerobic conditions. Significant exposure and accumulation in benthic systems is not anticipated, based upon the relatively limited potential of chlorsulfuron to move *via* run-off. Thus anaerobic degradation is predicted to play a very minor role in the environmental fate of chlorsulfuron.

Chlorsulfuron appears to be weakly adsorbed to soils in laboratory batch equilibrium studies and readily mobile in pre-wet column leaching studies, which represent worst-case field scenarios; yet an aged column leaching study, which represents a more probable field scenario, showed that chlorsulfuron and its major degradation products demonstrated much less mobility than might have been expected. Soil thin-layer chromatography demonstrated that the potential soil mobility of the major degradation products chlorobenzenesulfonamide (**2**) and triazine amine (**3**) was slightly and much less, respectively, than that of intact chlorsulfuron.

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